



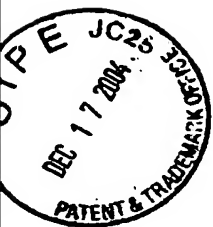
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For: POSITIVE ACTIVE MATERIAL FOR SECONDARY BATTERY, PROCESS FOR
PREPARATION THEREOF AND NON-AQUEOUS ELECTROLYTE SECONDARY
BATTERY COMPRISING SAME

SUBSTITUTE SPECIFICATION

SHOWING CHANGES



Description

POSITIVE ACTIVE MATERIAL FOR SECONDARY BATTERY, PROCESS FOR
PREPARATION THEREOF AND NON-AQUEOUS ELECTROLYTE SECONDARY
5 BATTERY COMPRISING SAME

Technical Field

The present invention relates to a positive active
material for a secondary battery, a process for the
10 preparation thereof and a non-aqueous electrolyte secondary
battery comprising the same.

Background Art

As a positive electrode for the non-aqueous
15 electrolyte secondary battery, there has been proposed a
lithium-transition metal oxide. As negative electrodes for
the non-aqueous electrolyte secondary battery, there has
been proposed graphite, ~~amorphous~~ low-crystalline carbon,
oxide, lithium alloy and metallic lithium. Nowadays,
20 lithium cobaltate (LiCoO_2) is mainly used as a positive
active material. However, this active material is
expensive. Accordingly, in order to cope with the expected
huge consumption of non-aqueous electrolyte secondary
batteries, development of less expensive positive active
25 materials is important.

Further, from the view point of the increasing interest in environmental issues, it is quite desirable that the active material is as environmentally friendly as possible. Nowadays, compounds containing manganese, nickel or iron are under extensive studies as the positive active materials for the non-aqueous electrolyte secondary battery. Among these elements, iron is the most inexpensive and environmentally friendly material. Thus, an iron compound is very attractive as a positive active material for the next-generation non-aqueous electrolyte secondary battery.

Various iron compounds have been heretofore proposed as iron-containing positive active materials for the non-aqueous electrolyte secondary battery. Among these iron compounds, iron oxyhydroxide (FeOOH), which is an active material delivering high capacity, has recently attracted much attention. Among several types of FeOOH with different crystalline structure, $\beta\text{-FeOOH}$ has a relatively large size of tunnel structure of (2×2) . It is expected that the use of $\beta\text{-FeOOH}$ as a positive active material for the non-aqueous electrolyte secondary battery would provide good battery properties.

Amine et al. investigated the positive-electrode characteristics in the secondary lithium cells using high-crystalline $\beta\text{-FeOOH}$ as a positive material. They reported that this active material exhibited an excellent charge-

discharge characteristics at a low current density of 0.1 mA/cm² (J. Power Sources, 81-82, 221 (1999)). However, the conventional high-crystalline β -FeOOH has a drawback of poor cycle-life performance at a higher current density.

5 An object of the present invention is to provide an inexpensive and environmentally friendly non-aqueous electrolyte secondary battery by using an unknown novel iron compound as a positive active material.

10 Disclosure of the Invention

 The positive active material of the invention is β -FeOOH comprising at least one element selected from the group consisting of B, P, S, Li, Na, K, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Zr, Pb and Sn, which shows a
15 diffraction peak from the (110) plane having a half width γ satisfying $0.3^\circ < \gamma$ (2 θ) when subjected to X-ray diffractometry with the CuK α ray. Defining that a material having a half width of not greater than 0.3° on the (110) peak is a high-crystalline material while a material having
20 a half width of greater than 0.3° on the (110) peak is an ~~amorphous~~-low crystalline material, β -FeOOH of the present invention is an ~~amorphous~~-low-crystalline one. The low-crystalline β -FeOOH shows a good cycle-life performance as compared with the high-crystalline one. Although this
25 phenomenon has not been clearly understood, it is considered that B, P, S, Li, Na, K, Mg, Al, Ca, Sc, Ti, V,

Cr, Mn, Co, Ni, Cu, Zn, Zr, Pb and Sn act as a column in the active material, resulting in the stabilization of the amorphous-low-crystalline structure. The reason why the half width γ on the (110) peak is restricted to the above defined range is that if the half width falls below this range, the active material becomes a high-crystalline compound, thus causing the poor cycle-life performance as mentioned before.

This positive active material is obtainable by adding a salt containing at least one element selected from the group consisting of B, P, S, Li, Na, K, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Zr, Pb and Sn to an aqueous solution in which an iron salt is dissolved, and then subjecting the resulting aqueous solution to hydrolysis at a temperature of from 40°C to 100°C. The aqueous solution used for the hydrolysis is preferably an acidic aqueous solution, particularly a hydrochloric acid solution.

In the case where the iron salt is ferric chloride (FeCl_3) and the vanadium salt is VOSO_4 , when an aqueous solution containing FeCl_3 and VOSO_4 dissolved therein at a molar ratio satisfying $0 < (\text{VOSO}_4/\text{FeCl}_3) < 0.1$ is subjected to hydrolysis at a temperature in the range of from 40°C to 100°C, aged for 1 day or longer, filtered, rinsed, and then dried, a positive active material of the present invention involving vanadium is prepared. The reason why the molar ratio of VOSO_4 to FeCl_3 is restricted to the above defined

range is that the molar ratio exceeding the above defined range gives a compound having a structure different from that of β -FeOOH.

Further, since the high-crystalline β -FeOOH is a
5 needle-like crystal having a great aspect ratio, the use of this material as an active material provides a reduced contact area between the particles. Accordingly, a large amount of an electrically-conducting agent is required to improve the electrical conductivity between the particles.
10 As a result, the density of the active material is lowered, which is disadvantage.

On the contrary, in accordance with the present invention which uses an ~~amorphous~~-low-crystalline β -FeOOH having a particle with an aspect ratio of not greater than
15 5, the particles can be packed densely, resulting in the improvement of the contact between the particles. Accordingly, the amount of the electrically-conducting agent to be added can be reduced, resulting in the increase in the density of the active material. Further, since the
20 contact area between the particles is large, good contact between the particles can be maintained even if the crystal lattice of the active material expands or shrinks. When the ~~amorphous~~-low-crystalline β -FeOOH having such properties is used as a positive active material for a non-
25 aqueous electrolyte secondary battery, the cycle-life performance of the resulting electrode can be remarkably

improved as compared with the conventional electrode having the high-crystalline β -FeOOH.

The ~~amorphous~~low-crystalline β -FeOOH of the present invention may be in the form of primary particle or
5 agglomerate of primary particles as long as the aspect ratio of particles having each form is not greater than 5. As long as the aspect ratio of the agglomerate is not greater than 5, the aspect ratio of the constituent primary particles may be not smaller than 5. Specific examples of
10 the crystal form of β -FeOOH of the present invention include column, cone, and rod.

The foregoing aspect ratio means the mean aspect ratio of individual particles. In some detail, 50 particles which are selected at random are observed under the
15 microscope. The average of the aspect ratios of the individual particles thus determined is defined as the aspect ratio of active material particles. Accordingly, an active material having an aspect ratio of not greater than 5 means that the average aspect ratio of the constituent
20 particles is not greater than 5.

The aspect ratio of individual particles indicates the degree of the slenderness of β -FeOOH particles, i.e., the ratio of (longer axis length/shorter axis length) of the particles. As the aspect ratio increases, the particle
25 becomes slender. In particular, when the aspect ratio of the particle is not greater than 2, the electrode

comprising the β -FeOOH exhibits a remarkably improved cycle-life performance.

Furthermore, the inventors made studies on the particle diameter of the ~~amorphous~~-low-crystalline β -FeOOH and its charge-discharge characteristics. As a result, it was found for the first time that a non-aqueous electrolyte secondary battery, comprising, as a positive active material, an ~~amorphous~~-low-crystalline β -FeOOH having a particle with a mode diameter of not greater than 10 μm and showing a diffraction peak from the (110) plane having a half width γ satisfying $0.3^\circ < \gamma (2\theta)$ when subjected to X-ray diffractometry with the $\text{CuK}\alpha$ ray exhibits an excellent cycle-life performance.

It is necessary that the mode diameter of this ~~amorphous~~-low-crystalline β -FeOOH particle is not greater than 10 μm , preferably not greater than 6 μm . The reason why the mode diameter is restricted to not greater than 10 μm is that, when the mode diameter is greater than this range, the active material exhibits a remarkably poor cycle-life performance. The term "mode diameter" as used herein means the maximum value on the particle-size distribution curve, i.e., the diameter of particles which are contained mostly in the powder, which is represented by D_{mod} (Kiichiro Kubo, "Funtai-Riron to Ouyou (Powder - Theory and Application)", Maruzen, 1979).

The particle may be in the form of primary particle, agglomerate of primary particles or mixture thereof. The mode diameter of primary particles or their agglomerate may be not greater than 10 μm . In the case where the positive
5 active material of the present invention is used in a non-aqueous electrolyte secondary battery, an agglomerate is preferred as the active material rather than primary particles. The reason is that the use of an agglomerate as an active material makes it possible to reduce the amount
10 of the electrically-conducting agent in the positive electrode, resulting in the further enhancement of the energy density of the battery.

When the ~~amorphous~~ low-crystalline $\beta\text{-FeOOH}$ of the invention is used as a positive active material for a
15 secondary lithium battery, the insertion/extraction of lithium occurs, resulting in the reduction of the crystallinity of the active material and a drastic change of the structure. The ~~amorphous~~ low-crystalline $\beta\text{-FeOOH}$ of the present invention which has been charged and discharged
20 shows new diffraction peaks at angles of about 19° , 26° and 32° when subjected to X-ray diffractometry with the $\text{CuK}\alpha$ ray. Then, the incorporation of at least one element selected from the group consisting of Li, Na, K, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Zr, Pb and Sn in
25 advance in the ~~amorphous~~ low-crystalline $\beta\text{-FeOOH}$ makes it possible to improve the cycle-life performance of the

battery. This is presumably because these elements act as columns in the crystal, exerting an effect of stabilizing the amorphous-low-crystalline structure.

Further, it is necessary that the amount of the foregoing elements in the amorphous-low-crystalline β -FeOOH of the invention is not smaller than 0.1 wt%. When the amount of these elements is not smaller than 0.1 wt%, the resulting cycle-life performance is remarkably improved. However, even when these elements are added in an amount exceeding the predetermined value, the improvement of the cycle-life performance is not observed. On the contrary, when the amount of these elements involved in the amorphous low-crystalline β -FeOOH increases, the discharge capacity decreases. Accordingly, the amount of these elements is preferably not smaller than 0.1 wt% but is as small as possible.

Brief Description of the Drawings

Fig. 1 is an exploded perspective view of a non-aqueous electrolyte secondary battery.

Fig. 2 is an enlarged sectional view of a positive electrode.

Fig. 3 is an enlarged sectional view of a negative electrode.

Fig. 4 illustrates X-ray diffraction patterns of the positive active materials used in the batteries A1 and A2 of the Examples and the comparative batteries B1 and B2.

5 Fig. 5 is a graph of the initial charge-discharge characteristics of the batteries A1 and A2 of the Examples and the comparative battery B1.

Fig. 6 is a graph illustrating the discharge capacity of the batteries A1 and A2 of the Examples and the comparative battery B1 at each cycle.

10 Fig. 7 illustrates X-ray diffraction patterns of the positive active material used in the battery A1 of the Example in the charged state (a), in the discharged state (b) and before charge and discharge (c), wherein the symbol * indicates new diffraction peaks which appear during the
15 charge and discharge.

Fig. 8 illustrates a X-ray diffraction pattern of the positive active material used in the battery A3 of the Example.

20 Fig. 9 is a scanning electron microphotograph of the positive active material used in the battery A3 of the Example.

Fig. 10 is a graph illustrating the discharge capacity of the battery A3 of the Example and the comparative battery B1 at each cycle.

Fig. 11 is a graph illustrating the relationship between the amount of the electrically-conducting agent and the discharge capacity at the 10th cycle.

Fig. 12 is a graph illustrating the relationship
5 between the retention of the discharge capacity and the amount of Al in the particle of the positive active material.

Fig. 13 is a graph illustrating the relationship between the retention of the discharge capacity and the
10 mode diameter of the particle of the positive active material.

Best Mode for Carrying Out the Invention

Preferred embodiments of the present invention will be
15 described hereinafter.

An example of the process for the preparation of an ~~amorphous~~low-crystalline β -FeOOH of the present invention is explained as follows. It is obtained by adding a salt containing at least one element selected from the group
20 consisting of B, P, S, Li, Na, K, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Zr, Pb and Sn to an aqueous solution in which an iron salt dissolved, and subjecting the resulting solution to hydrolysis at a temperature of from 40°C to 100°C. The aqueous solution used for the
25 hydrolysis is preferably an acidic aqueous solution, particularly a hydrochloric acid solution. As the salt to

be added, a sulfate is particularly preferred. The reason why a sulfate is particularly preferred is that the use of a sulfate makes it possible to remarkably enhance the yield. It is preferred that the product obtained by the hydrolysis is aged for 1 day or longer, filtered, rinsed, and dried. This preparation process is extremely simple and very excellent as an industrial process.

Examples of the iron salt to be used in the process for the preparation of the positive active material of the present invention include FeO , Fe_2O_3 , Fe_3O_4 , FeBr_2 , FeBr_3 , FeCl_2 , FeCl_3 , $\text{Fe}(\text{NO}_3)_3$, $\text{Fe}_3(\text{PO}_4)_2$, FePO_4 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{C}_2\text{O}_4)$, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, and $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$. Examples of the salt containing B, P, S, Li, Na, K, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Zr, Pb, or Sn include NaBO_2 , $\text{Na}_4\text{B}_2\text{O}_5$, $\text{Na}_2\text{B}_4\text{O}_7$, NaB_5O_8 , $\text{Na}_2\text{B}_6\text{O}_{10}$, $\text{Na}_2\text{B}_8\text{O}_{13}$, Na_2HPO_4 , Na_2HPO_3 , NaBr , NaBrO_3 , NaCl , NaClO_3 , NaI , NaNO_3 , Na_3PO_4 , NaPO_3 , $\text{Na}_4\text{P}_2\text{O}_7$, LiBr , LiCl , LiI , LiNO_3 , Li_2SO_4 , Na_2SO_4 , Na_2S , NaOH , KBr , KBrO_3 , K_2CO_3 , $\text{K}_2\text{C}_2\text{O}_4$, KCl , KI , KNO_3 , K_3PO_4 , $\text{K}_4\text{P}_2\text{O}_7$, $\text{KCr}(\text{SO}_4)_2$, KOH , K_2S , MgBr_2 , $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$, MgCl_2 , MgI_2 , $\text{Mg}_3(\text{PO}_4)_2$, MgSO_4 , AlCl_3 , $\text{Al}(\text{NO}_3)_3$, $\text{Al}_2(\text{SO}_4)_3$, CaBr_2 , CaCl_2 , CaI_2 , $\text{Ca}(\text{NO}_3)_2$, ScCl_3 , $\text{Sc}_2(\text{SO}_4)_3$, TiBr_4 , TiCl_4 , $\text{Ti}(\text{SO}_4)_2$, TiOSO_4 , VOCl_3 , VOSO_4 , CrBr_3 , CrCl_3 , $\text{Cr}_2(\text{SO}_4)_3$, MnBr_2 , MnCl_2 , $\text{Mn}(\text{NO}_3)_2$, MnSO_4 , CoBr_2 , CoCl_2 , CoI_2 , $\text{Co}(\text{NO}_3)_2$, CoSO_4 , NiBr_2 , $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$, NiCl_2 , NiI_2 , $\text{Ni}(\text{NO}_3)_2$, NiSO_4 , CuBr_2 , $\text{Cu}(\text{CH}_3\text{COO})_2$, CuCl_2 , $\text{Cu}(\text{NO}_3)_2$, CuSO_4 , ZnBr_2 , $\text{Zn}(\text{CH}_3\text{COO})_2$, ZnCl_2 , ZnI_2 , $\text{Zn}(\text{NO}_3)_2$, ZnSO_4 , ZrCl_4 , ZrI_4 , ZrOCl_2 , $\text{Zr}(\text{SO}_4)_2$, $\text{Pb}(\text{CH}_3\text{COO})_2$,

$\text{Pb}(\text{NO}_3)_2$, SnBr_2 , SnCl_2 , SnCl_4 , SnF_2 , SnF_4 , and SnSO_4 . These salts may be used in the form of a hydrate and may be used singly, or two or more of these salts may be used in admixture.

5 When the positive active material of the present invention is used to form a non-aqueous electrolyte secondary battery, structures as shown in Figs. 1 to 3 may be used. That is, a positive electrode 10 and a negative electrode 20 are spirally wound with a separator 30 of a
10 nonwoven polyethylene fabric therebetween. The spirally laminated electrode element 40 thus obtained is inserted in a battery case 41. The battery case 41 comprises a negative electrode case 42 in the form of cylindrical vessel, and the opening of the cylindrical vessel is closed
15 by a positive electrode cap 43. Though not shown, the interior of the battery case is filled with a liquid non-aqueous electrolyte.

 The aforementioned positive electrode 10 has a structure comprising a positive-electrode composite 12
20 retained on both sides of a current collector 11 of an aluminum foil having a thickness of, for example, 20 μm as shown in Fig. 2. The positive electrode 10 is obtained by adding, for example, a binder or electrically-conducting agent, etc., to a positive active material of the present
25 invention, spreading the resulting paste on both sides of the current collector 11, drying the coated material, and

then pressing the dried material. The positive electrode 10 is then cut into a belt having a predetermined width before use. On the other hand, as shown in Fig. 3, the foregoing negative electrode 20 has a structure comprising a negative-electrode composite 22 retained on both sides of a current collector 21 of, e.g., a copper foil. The negative electrode 20 is obtained by mixing a negative active material with a binder, spreading the resulting paste on both sides of the current collector 21, drying the coated material, and then pressing the dried material. The negative electrode 20 is then cut into a belt having a predetermined width before use. The belt-shaped positive and negative electrodes are spirally wound with the foregoing separator 30 therebetween.

As the negative material to be used in the non-aqueous electrolyte secondary battery of the present invention, there may be used a material capable of inserting and extracting lithium ion and/or metallic lithium. Examples of the material capable of inserting and extracting lithium ion include graphites, ~~amorphous~~ low-crystalline carbons, oxides, nitrides, and lithium alloys. Examples of the lithium alloys include alloys of lithium and metals such as aluminum, zinc, bismuth, cadmium, antimony, silicon, lead, and tin.

The non-aqueous electrolyte to be used in the non-aqueous electrolyte secondary battery of the present

invention may be in the form of any of a non-aqueous electrolytic solution, a polymer electrolyte and a solid electrolyte. Examples of the solvent to be used in the non-aqueous electrolytic solution include polar solvents
5 such as ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, methyl ethylene carbonate, γ -butyrolactone, sulfolan, dimethyl sulfoxide, acetonitrile, dimethylformamide, dimethylacetamide, 1,2-dimethoxyethane, 1,2-diethoxyethane, tetrahydrofuran, 2-
10 methyltetrahydrofuran, dioxolane and methyl acetate, and mixture thereof. Examples of the solute to be dissolved in the solvent include salts such as LiPF_6 , LiBF_4 , LiAsF_6 , LiClO_4 , LiSCN , LiCF_3CO_2 , LiCF_3SO_3 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$, $\text{LiN}(\text{COCF}_3)_2$ and $\text{LiN}(\text{COCF}_2\text{CF}_3)_2$, and mixture
15 thereof.

The non-aqueous electrolyte secondary cell comprising an ~~amorphous~~ low-crystalline β -FeOOH as a positive active material will be further described in the following Examples.

20 [Example 1]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.0066 mole of TiBr_4 were together dissolved in 1 dm^3 of water at a temperature of 25°C . Subsequently, this solution was heated at a rate as low as about $10^\circ\text{C}/\text{h}$, and then kept at a temperature of 85°C
25 for 2 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a

temperature of 80°C to obtain a positive active material of the present invention.

Subsequently, to 75 weight percent of the foregoing positive active material were added 20 weight percent of acetylene black and 5 weight percent of poly(vinylidene fluoride) (PVDF). The mixture was then mixed with N-methyl-2-pyrrolidone in a wet process to form a slurry. The slurry thus obtained was then spread on both sides of an aluminum mesh as a current collector. The electrode thus obtained was then dried at a temperature of 80°C. Further, the electrode was pressed at 1 t/cm², and then dried in vacuo at a temperature of 100°C to prepare a positive electrode having a size of 15 mm x 15 mm x 0.5 mm.

Finally, the foregoing positive electrode was used to prepare a cell (A1) of this Example comprising a positive active material of the present invention. The flooded-type cell comprises metallic lithium as a negative electrode and a 1 : 1 (by volume) mixture of ethylene carbonate and dimethyl carbonate having 1 mol/l of LiClO₄ dissolved therein as a non-aqueous electrolytic solution.

[Example 2]

0.1 mole of FeCl₃·6H₂O and 0.0033 mole of VOSO₄·2H₂O were together dissolved in 1 dm³ of water at a temperature of 25°C. Subsequently, this aqueous solution was heated at a rate as low as 10°C/h, and then kept at a temperature of 80°C for 2 days. The resulting precipitate was filtrated,

thoroughly washed with distilled water, and then dried at a temperature of 80°C to obtain a positive active material of the present invention.

Finally, a cell (A2) of this Example was prepared in the same manner as in Example 1 except that the foregoing positive active material was used.

[Comparative Example 1]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 1 dm³ of water at a temperature of 25°C. Subsequently, this aqueous solution was heated at a rate as low as 10°C/h, and then kept at a temperature of 60°C for 2 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a temperature of 80°C to obtain a positive active material.

Finally, a comparative cell (B1) was prepared in the same manner as in Example 1 except that the foregoing positive active material was used.

[Comparative Example 2]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.012 mole of $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ were together dissolved in 1 dm³ of water at a temperature of 25°C. Subsequently, this aqueous solution was heated at a rate as low as 10°C/h, and then kept at a temperature of 70°C for 2 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a temperature of 80°C to obtain a positive active material.

Finally, a comparative cell (B2) was prepared in the same manner as in Example 1 except that the foregoing positive active material was used.

Figs. 4A, B, C and D indicate X-ray diffraction patterns (the $\text{CuK}\alpha$ ray) of the positive active materials used in the comparative cells B1 and B2 and the cells A1 and A2 of the present invention, respectively. From the position of the diffraction peaks, it was found that the active materials used in the cells A1 and A2 of the Examples and the comparative cell B1 were $\beta\text{-FeOOH}$. On the other hand, the active material used in the comparative cell B2 was found to have a structure quite different from that of $\beta\text{-FeOOH}$.

The ICP spectroscopy revealed that the positive active material used in the cell A1 and that used in the cell A2 of the Examples contained about 3 wt% of Ti and V, respectively. On the other hand, the positive active material used in the comparative cell B2 was found to contain about 25 wt% of V.

Comparing the cell A2 of the Example with the comparative cell B2, the active material used in the former cell was obtained under the condition of $\text{VOSO}_4/\text{FeCl}_3$ (molar ratio) < 0.1 while the active material used in the latter cell was synthesized under the condition of $\text{VOSO}_4/\text{FeCl}_3$ (molar ratio) > 0.1 . It was thus found that the hydrolysis of an aqueous solution in which FeCl_3 and VOSO_4 are

dissolved at a molar ratio satisfying

$0 < (\text{VOSO}_4/\text{FeCl}_3) < 0.1$ makes it possible to obtain an
~~amorphous~~-low-crystalline β -FeOOH of the present invention.

The values of the half width of a diffraction peak
5 from the (110) plane for the active materials used in the
cells A1 and A2 of the Examples and the comparative cell B1
were about 0.5° , 1.2° , and 0.2° , respectively. It was thus
found that the positive active materials used in the cells
A1 and A2 of the Examples and the active material used in
10 the comparative cell B1 were ~~amorphous~~-low-crystalline β -
FeOOH and high-crystalline β -FeOOH, respectively.

[Charge-discharge characteristics]

The cells A1 and A2 of the Examples and the
comparative cells B1 and B2 thus prepared were each
15 subjected to the 10-cycle charge-discharge test at a
constant current. The termination voltages for the charge
and discharge were 4.3 V and 1.6 V, respectively.

Fig. 5 illustrates the initial charge-discharge
characteristics of the cells of the Examples and the
20 comparative cells. Fig. 6 illustrates the discharge
capacity of the cells of the Examples and the comparative
cells at each cycle. In these Figs., the symbols \bullet , \blacktriangle ,
and \square indicate the characteristics of the cell A1 of the
Example, the cell A2 of the Example, and the Comparative
25 cell B1, respectively. The discharge capacity herein is

represented by electricity per 1 g of the positive active material (mAh/g).

Fig. 5 illustrates the initial charge-discharge characteristics of the cells of the Examples and the comparative cells. The current was 0.1 mA/cm^2 . The cells of the Examples exhibit the higher charge and discharge capacities as compared with the comparative cells, indicating that the cells of the Examples provide the better charge-discharge characteristics.

Fig. 6 illustrates the discharge capacity of the cells of the Examples and the comparative cells at each cycle. The current was 0.2 mA/cm^2 . It was apparent that the cells of the Examples show the better cycle-life performance than the comparative cells.

The cell A1 of the Example was charged at 4.3 V or discharged at 1.6 V, and then disassembled. The positive active material used was then subjected to X-ray diffractometry. The X-ray diffraction patterns of the products after charge and discharge are shown in Figs. 7A and B, respectively. The X-ray diffraction pattern of the active material used in the cell A1 of the Example before charge and discharge is shown in Fig. 7C. Comparing Figs. 7A, B with Fig. 7C, it can be seen that, after charge and discharge, the intensity of the diffraction peaks of the active material is remarkably lowered and that new diffraction peaks appear at the angles of about 19° , 26°

and 32°. Furthermore, Fig. 7B shows that new diffraction peaks appear at the angles of about 43° and 63° for the cell in the discharged state. From these results, it was found that when an ~~amorphous~~-low-crystalline β -FeOOH is used as a positive active material of the present invention for the secondary lithium cell, the insertion/extraction of lithium occurs, which further lowers the crystallinity of the β -FeOOH and hence causes a drastic change of its structure. The high-intensity peaks observed at the angles of about 38°, 45° and 65° in Figs. 7A and B are attributed to aluminum used as a current collector.

[Example 3]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.1 mole of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were together dissolved in 1 dm³ of water at a temperature of 25°C. Subsequently, this solution was heated at a rate as low as 10°C/h, and then kept at a temperature of 80°C for 2 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a temperature of 80°C to obtain a positive active material of the present invention.

Finally, a positive electrode and a cell (A3) of this Example were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 70 weight percent, 20 weight percent and 10 weight percent, respectively.

[Example 4]

A positive active material of the present invention was obtained in the same manner as in Example 3.

Subsequently, a positive electrode and a cell (A4) of this Example were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 75 weight percent, 15 weight percent and 10 weight percent, respectively.

[Example 5]

A positive active material of the present invention was obtained in the same manner as in Example 3.

Subsequently, a positive electrode and a cell (A5) of this Example were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 80 weight percent, 10 weight percent and 10 weight percent, respectively.

[Example 6]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.033 mole of $\text{Al}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ were together dissolved in 1 dm^3 of water at a temperature of 25°C . Subsequently, this solution was heated at a rate as low as 10°C/h , and then kept at a temperature of 80°C for 2 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a

temperature of 80°C to obtain a positive active material of the present invention.

Finally, a positive electrode and a cell (A6) of this Example were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 80 weight percent, 10 weight percent and 10 weight percent, respectively.

[Example 7]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.04 mole of $\text{Al}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ were together dissolved in 1 dm³ of water at a temperature of 25°C. Subsequently, this solution was heated at a rate as low as 10°C/h, and then kept at a temperature of 80°C for 2 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a temperature of 80°C to obtain a positive active material of the present invention.

Finally, a positive electrode and a cell (A7) of this Example were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 80 weight percent, 10 weight percent and 10 weight percent, respectively.

[Example 8]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.05 mole of $\text{Al}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ were together dissolved in 1 dm³ of water at a temperature

of 25°C. Subsequently, this solution was heated at a rate as low as 10°C/h, and then kept at a temperature of 85°C for 2 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a temperature of 80°C to obtain a positive active material of the invention.

Finally, a positive electrode and a cell (A8) of this Example were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 80 weight percent, 10 weight percent and 10 weight percent, respectively.

[Comparative Example 3]

A positive active material was obtained in the same manner as in Comparative Example 1. Subsequently, a positive electrode and a comparative cell (B3) were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 70 weight percent, 20 weight percent and 10 weight percent, respectively.

[Comparative Example 4]

A positive active material was obtained in the same manner as in Comparative Example 1. Subsequently, a positive electrode and a comparative cell (B4) were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene

black and PVdF used were 75 weight percent, 15 weight percent and 10 weight percent, respectively.

[Comparative Example 5]

5 A positive active material was obtained in the same manner as in Comparative Example 1. Subsequently, a positive electrode and a comparative cell (B5) were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 80 weight percent, 10 weight
10 percent and 10 weight percent, respectively.

[Comparative Example 6]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.02 mole of $\text{Al}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ were together dissolved in 1 dm^3 of water at a temperature of 25°C. Subsequently, this solution was heated at a rate
15 as low as 10°C/h, and then kept at a temperature of 80°C for 2 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a temperature of 80°C to obtain a positive active material.

Finally, a positive electrode and a comparative cell
20 (B6) were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 80 weight percent, 10 weight percent and 10 weight percent, respectively.

[Comparative Example 7]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.025 mole of $\text{Al}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ were together dissolved in 1 dm³ of water at a temperature of 25°C. Subsequently, this solution was heated at a rate as low as 10°C/h, and then kept at a temperature of 80°C for 2 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a temperature of 80°C to obtain a positive active material.

Finally, a positive electrode and a comparative cell (B7) were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 80 weight percent, 10 weight percent and 10 weight percent, respectively.

Fig. 8 shows the X-ray diffraction pattern (the $\text{CuK}\alpha$ ray) of the positive active material used in the cell A3 of the Example. From the position of the diffraction peaks in Fig. 8, the active material used in the cell A3 of the Example was found to be $\beta\text{-FeOOH}$. The half width of the diffraction peak from the (110) plane for the active material used in the cell A3 was about 0.7°. These results indicate that the positive active material used in the cell A3 of the Example was an ~~amorphous~~ low-crystalline $\beta\text{-FeOOH}$. As previously mentioned, the active material used in the comparative cell B3 is a high-crystalline $\beta\text{-FeOOH}$.

The lattice constants of the tetragonal β -FeOOH determined from the position of the X-ray diffraction peaks were $a = 10.50 \text{ \AA}$ and $c = 3.03 \text{ \AA}$ for the ~~amorphous-low-crystalline~~ β -FeOOH used in the cell A3 of the Example, and $a = 10.54 \text{ \AA}$ and $c = 3.03 \text{ \AA}$ for the high-crystalline β -FeOOH. It was thus found that the unit cell of the ~~amorphous-low-crystalline~~ β -FeOOH of the present invention has shrunk in the direction of the a-axis as compared with that of the high-crystalline one.

Fig. 9 illustrates the scanning electron microphotograph of the positive active material used in the cell A3 of the Example. The active material used in the cell A3 of the Example was found to comprise particles having an average diameter of about $4 \text{ }\mu\text{m}$ and an aspect ratio of not greater than 2. On the other hand, the active material used in the comparative cell B3 was found to comprise needle-like particles having an aspect ratio of about 8; the length of a longer axis was about $0.8 \text{ }\mu\text{m}$ and that of a shorter axis was about $0.1 \text{ }\mu\text{m}$.

The ICP spectroscopy confirmed that β -FeOOH used in the cell A3 of the Example contained 0.07 wt% of Cu.

The cell A3 of the Example was charged, discharged, disassembled, and then subjected to the X-ray diffractometry of the positive active material in the same manner as the cell A1 of the Example. The resulting products after charge and discharge showed the X-ray

diffraction patterns similar to those shown in Figs. 7A and B, respectively.

[Charge-discharge characteristics]

The cells A3, A4 and A5 of the Examples and the comparative cells B3, B4 and B5 thus prepared were each then subjected to the 10-cycle charge-discharge test with a constant current. The termination voltages for the charge and discharge were 4.3 V and 1.6 V, respectively. The current was 0.2 mA/cm².

Fig. 10 illustrates the discharge capacities of the cell A3 of the Example and the comparative cell B3 at each cycle. In Fig. 10, the symbols ■ and ○ indicate the discharge capacities of the cell A1 of the Example and the comparative cell B3 at each cycle, respectively. From Fig. 10, it was found that the cell of the Example shows better cycle-life performance than the comparative cell.

Fig. 11 illustrates the relationship between the amount of acetylene black added as an electrically-conducting agent and the discharge capacity at the 10th cycle for the cells A3, A4 and A5 of the Examples and the comparative cells B3, B4 and B5. In Fig. 11, the symbol ■ indicates the values for the cells A3, A4 and A5 of the Examples and the symbol ○ indicates those for the comparative cells B3, B4 and B5. From Fig. 11, it was found that the cells of the Examples give a higher discharge capacity than the comparative cells even if the

amount of the electrically-conducting agent in the positive electrode is small.

Subsequently, β -FeOOH having different aspect ratios were used to prepare cells similar to that used in the Example 3. The prepared cells were then subjected to the charge-discharge cycling test in the same manner as in Example 3. The 10th discharge capacities are shown in Table 1. The values of the discharge capacities in Table 1 were averaged ones calculated from the 10 cells.

Table 1

Aspect ratio	Discharge capacity (mAh/g)
1.5	165
1.9	161
2.8	154
3.5	152
4.6	151
5.9	142
6.4	138
7.9	133

As is clearly seen in Table 1, the aspect ratio of β -FeOOH which is not greater than 5 showed the discharge capacity over 150 mAh/g. In particular, when the aspect ratio of β -FeOOH is not greater than 2, the discharge capacity exceeds 160 mAh/g.

When subjected to the ICP spectroscopy, the active materials used in the cells A6, A7 and A8 of the Examples and the comparative cells B6 and B7 were found to contain

Al. Then, the relationship between the amount of Al and the charge-discharge characteristics was examined.

Scanning electron microscopy confirmed that the active materials used in the cells A6, A7 and A8 of the Examples and the comparative cells B6 and B7 had an aspect ratio of not greater than 5.

Fig. 12 illustrates the relationship between the retention of the discharge capacities of the cells A6, A7 and A8 of the Examples and the comparative cells B6 and B7 at the 10th cycle and the amount of Al in the active materials used in these cells. The "retention of the discharge capacity" is defined by the ratio of the discharge capacity at the 10th cycle to the initial discharge capacity. The value of the retention is shown by percentage. It is clearly seen that, when the amount of Al in the active material is not smaller than 0.1 wt%, the resulting cells show a remarkably high retention of the discharge capacity.

The cell A3 of the Example was charged at 4.3 V or discharged at 1.6 V, and then disassembled. The positive active material used was then subjected to X-ray diffractometry. The resulting products after charge and discharge showed the X-ray diffraction patterns similar to those shown in Figs. 7A and B. This result indicates that when an ~~amorphous~~ low-crystalline β -FeOOH of the present invention having a particle with an aspect ratio of not

greater than 5 is used as a positive active material for the secondary lithium cell, the insertion/extraction of lithium occurs, which further lowers the crystallinity of β -FeOOH and hence causes a drastic change of its structure.

5 [Example 9]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.0033 mole of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ were together dissolved in 1 dm^3 of water at a temperature of 25°C. Subsequently, this solution was heated at a rate as low as 10°C/h, and then kept at a temperature of 60°C
10 for 2 days. The resulting precipitate filtrated, thoroughly washed with distilled water, and then dried at a temperature of 80°C to obtain a positive active material of the present invention.

Finally, a positive electrode and a cell (A9) of this
15 Example were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 80 weight percent, 10 weight percent and 10 weight percent, respectively.

20 [Example 10]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.05 mole of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ were together dissolved in 1 dm^3 of water at a temperature of 25°C. Subsequently, this solution was heated at a rate as low as 10°C/h, and then kept at a temperature of 70°C for 2
25 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a

temperature of 80°C to obtain a positive active material of the present invention.

Finally, a positive electrode and a cell (A10) of this Example were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 80 weight percent, 10 weight percent and 10 weight percent, respectively.

[Example 11]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.1 mole of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ were together dissolved in 1 dm³ of water at a temperature of 25°C. Subsequently, this solution was heated at a rate as low as 10°C/h, and then kept at a temperature of 90°C for 2 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a temperature of 80°C to obtain a positive active material of the present invention.

Finally, a positive electrode and a cell (A11) of this Example were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 80 weight percent, 10 weight percent and 10 weight percent, respectively.

[Example 12]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.01 mole of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ were together dissolved in 1 dm³ of water at a temperature of

25°C. Subsequently, this solution was heated at a rate as low as 10°C/h, and then kept at a temperature of 60°C for 2 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a
5 temperature of 80°C to obtain a positive active material of the present invention.

Finally, a positive electrode and a cell (A12) of this Example were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active
10 material, acetylene black and PVdF used were 80 weight percent, 10 weight percent and 10 weight percent, respectively.

[Example 13]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.033 mole of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ were
15 together dissolved in 1 dm³ of water at a temperature of 25°C. Subsequently, this solution was heated at a rate as low as 10°C/h, and then kept at a temperature of 60°C for 2 days. The resulting precipitate was filtrated, thoroughly washed with distilled water, and then dried at a
20 temperature of 80°C to obtain a positive active material of the present invention.

Finally, a positive electrode and a cell (A13) of this Example were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active
25 material, acetylene black and PVdF used were 80 weight

percent, 10 weight percent and 10 weight percent,
respectively.

[Comparative Example 8]

0.1 mole of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.03 mole of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were
5 together dissolved in 1 dm³ of water at a temperature of
25°C. Subsequently, this solution was heated at a rate as
low as 10°C/h, and then kept at a temperature of 60°C for 2
days. The resulting precipitate was filtrated, thoroughly
washed with distilled water, and then dried at a
10 temperature of 80°C to obtain a positive active material.

Finally, a positive electrode and a comparative cell
(B8) were prepared in the same manner as in Example 1
except that the amount of the foregoing positive active
material, acetylene black and PVdF used were 80 weight
15 percent, 10 weight percent and 10 weight percent,
respectively.

[Comparative Example 9]

A positive active material of the present invention
was obtained in the same manner as in Example 9.
20 Subsequently, a positive electrode and a comparative cell
(B9) were prepared in the same manner as in Example 1
except that the amount of the foregoing positive active
material, acetylene black and PVdF used were 70 weight
percent, 20 weight percent and 10 weight percent,
25 respectively.

[Comparative Example 10]

A positive active material of the present invention was obtained in the same manner as in Example 10.

Subsequently, a positive electrode and a comparative cell (B10) were prepared in the same manner as in Example 1 except that the amount of the foregoing positive active material, acetylene black and PVdF used were 70 weight percent, 20 weight percent and 10 weight percent, respectively.

The positive active materials used in the cells A9 to A13 of the Examples and those used in the comparative cells B8 to B10 showed X-ray diffraction patterns similar to that shown in Fig. 8. This result indicates that the active materials used in the cells A9 to A13 of the Examples and those used in the comparative cells B8 to B10 were all ~~amorphous~~ low-crystalline β -FeOOH.

Table 2 shows the mode diameter of the positive active materials determined by the particle-size analysis for the cells A9 to A13 of the Examples and the comparative cell B8.

Table 2

Cell No.	Mode diameter of particle (μm)
A9	0.6
A10	3.4
A11	5.1
A12	6.2
A13	9.5
B8	13.9

As can be seen in Table 2, all the particles of the active materials used in the cells A9 to A13 of the Examples had a mode diameter of not greater than 10 μm . SEM observation confirmed that the active material used in the cell A9 of the Example was mainly composed of primary particles and that those used in the cells A10 to A13 of the Examples were found to be mainly composed of agglomerates of primary particles.

[Charge-discharge characteristics]

The cells A9 to A13 of the Examples and the comparative cells B8 to B10 thus prepared were then subjected to the 10-cycle charge-discharge test with a constant current. The termination voltages for the charge and discharge were 4.3 V and 1.6 V, respectively. The current was 0.2 mA/cm^2 . The measurement was conducted at a temperature of 25°C.

Fig. 13 illustrates the relationship between the retention of the 10th discharge capacities of the cells A9 to A13 of the Examples and the comparative cells B8 and the

mode diameter of the particles of the positive active materials used in these cells.

As can be seen in Fig. 13, when the mode diameter of the particle of the active material is not greater than 10 μm , particularly not greater than 6 μm , the resulting cell exhibits a remarkably high retention of the discharge capacity.

From the particle-size analysis, the active materials used in the cells A6, A7 and A8 of the Examples and those used in the comparative cells B6 and B7 were found to have particles with a mode diameter of from 3 μm to 5 μm . Accordingly, taking into account the relationship shown in Fig. 12, it was clarified that when an ~~amorphous~~ low-crystalline $\beta\text{-FeOOH}$, which has a mode diameter of not greater than 10 μm and the amount of Al of not smaller than 0.1 wt%, is used as a positive active material, the resulting cell shows a remarkably high retention of the discharge capacity.

In the Examples 9 to 13, the active material, acetylene black and PVdF was mixed with a ratio of 80 : 10 : 10 in weight. Subsequently, the effect of the amount of the electrically-conducting agent on the charge-discharge characteristics was examined. The comparative cells B9 and B10 containing the active material, acetylene black, and PVdF with a weight ratio of 70 : 20 : 10 were subjected to the charge-discharge test. The results were then compared

with those of the cells A9 and A10 of the Examples. As a result, the retentions of the 10th discharge capacities were similar between the comparative cells B9 and B10. On the other hand, when the amount of the electrically-
5 conducting agent is 10 wt%, the cell A10 of the Example showed a higher retention of the discharge capacity than the cell A9 of the Example as shown in Fig. 13. The active material used in the cell A9 of the Example is mainly composed of primary particles while the active material
10 used in the cell A10 of the Example is mainly composed of agglomerates. From these facts, it was found that when an agglomerate is used as an active material, a high discharge capacity can be retained even if the amount of the electrically-conducting agent is reduced.

15 In the present Examples, metallic lithium was used as a negative electrode material. When a compound comprising a positive active material of the present invention which contains lithium is used as a positive active material, graphite, ~~amorphous~~low-crystalline carbon, oxide, nitride,
20 lithium alloy or the like may be used as a negative electrode material. As a method to insert lithium in the active material of the present invention, there may be exemplified a chemical process besides the electrochemical process described in the foregoing Examples. An example of
25 the chemical process includes a method involving the

reaction of the active material of the invention with a reducing agent such as n-BuLi and LiI.

Industrial Possibility

5 As mentioned above, in accordance with the invention, the use of an unknown novel iron compound as a positive active material makes it possible to provide an inexpensive and environmentally friendly non-aqueous secondary battery.